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Pilot-scale experimentation supplies the performance data necessary for industrial extrapolation. It requires pilot plants in which thermal and matter transfers are fully controlled given extrapolation factors in the region of 10^5 to 10^6 between a pilot reactor and an industrial unit reactor. In addition, the increased demand for more eco-efficient processes requires the use of intensified, instrumented and digitalized pilot plants. In this context, the Process Experiments Division has designed and operates a fleet of nearly 80 installations covering all of IFPEN's processes.

To develop project support expertise, the division draws on fundamental research focused on both the characterization of materials and fluids and the modeling of closely coupled phenomena with a view to scale change. This issue presents a few of the key achievements resulting from such research.

An emerging research challenge is the use of data sciences. This will enable us to rethink the management and operation of pilot plant tests with a view to enhanced efficiency for IFPEN's R&I.

I hope you enjoy reading this issue.

Denis Guillaume,
Director of the Process Experiments
Division

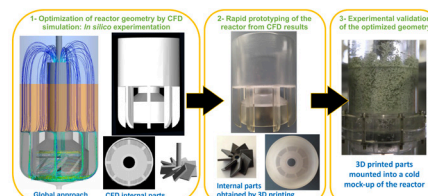
CFD and 3D are causing a stir in the world of reactors

In order to develop and test new processes for the production of responsible fuels or bio-based chemical intermediates, complex and miniature reactors for IFPEN pilot units have been developed and produced using an innovative method, where traditional design and manufacturing ones are not suitable for obtaining appropriate geometries.

The new methodology is based on CFD (Computational Fluid Dynamics) to design and optimize the geometry⁽¹⁾ then on 3D printing techniques to make the reactor. It has been applied to design a stirred tank reactor that can be used for gas/liquid chemical reactions, in the presence of solid catalytic particles. The latter, contained inside a basket closed by grids, are suspended by the flow, thereby forming a catalytic ebullating bed.

Optimization of the basket geometry is obtained by interactive combination of simulation, production of a prototype by 3D printing and experimental validation on models. Finally, the optimized reactor is manufactured by metal 3D printing (figure).

This approach that is simultaneously economical and highly reactive can be used to rapidly design and produce innovative reactors. It thus paves the way for new opportunities for the design



Three-phase stirred tank reactor: from CFD (left) to technological reality (right).

of chemical reactors. Currently applied in experimental facilities, it could be extended to an industrial scale in the near future, once additive manufacturing has reached the standards required for certification of components. ■

* - The orange area shows the catalytic ebullating bed area

(1) V. Santos-Moreau, L. Brunet-Errard, M. Rolland, Numerical CFD simulation of a batch stirred tank reactor with stationary catalytic basket, *Chem. Eng. J.*, Vol. 207-208, 2012, pages 596-606, ISSN 1385-8947. DOI: 10.1016/j.cej.2012.07.020

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Raman: the secret of a successful separation

The development and optimization of chemical processes increasingly involves the instrumentation of pilot and industrial units with inline effluent analysis technologies, capable of supplying relevant, rapid and reliable information. In addition, the miniaturization of pilot tools has led researchers to study the contribution of spectral analysis solutions requiring no sampling, while ensuring the rapid availability of data on multifold schematics, without disrupting media.

Hence Raman^a spectrometry has proved to be a relevant method, capable of supplying spectra offering a wealth of chemical information⁽¹⁾. Furthermore, the use of fiber optics enables the use of a remote analyzer. Combined with this technique, chemometrics make it possible to predict the amount of each component of the analyzed mixture from the spectrum obtained.

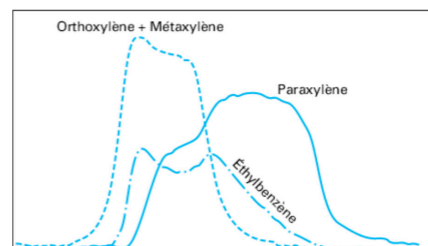
During the construction of a pilot facility for a new eco-efficient xylene separation process, Raman technology was chosen⁽²⁾ for the remote measurement of

the concentrations of the various aromatic compounds, including paraxylene^b.

The system is composed of a laser, optical fibers, multiplexed probes, a spectrometer and a computer with integrated analysis software and predictive models. Integrated probes are used to perform direct measurement in the fluid flow, on very low quantities of product, without sampling.

This is a winning choice in terms of real-time access to the concentrations of the components used in the process (figure), on three flows simultaneously, without destabilizing the flows.

Using this solution, the concentration profiles of various hydrocarbons can be obtained in real time, making it possible to monitor and optimize the separation process, saving precious time in terms of the overall process. ■



Concentration profiles during xylene separation^c.

- a - Non-destructive optical method to observe and characterize the molecular composition and external structure of a material.
- b - A key intermediate in the manufacture of PET (plastic bottles, textiles, etc.).
- c - A complete recording every 15 minutes.

[1] P. Marteau, N. Zanier-Szydłowski, A. Aoufi, G. Hotier, F. Cansell, *Remote Vibrational Spectroscopy* 1995.

DOI: 10.1016/0924-2031(94)00050-Q

[2] D. Gonçalves, M. Lacoue-Nègre, M. Josserand, O. Delpoux, C. Laroche, J. Pérez Pellitero, *Chimie 2018; CNAM, Paris, 30-31/01/2018*

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Processes are converting to microfluidics

The diversification of resources (atypical oil feeds or bio-based feeds) is leading to the development of new conversion processes^a or to the upgrading of flexibility for existing ones. These developments require precise knowledge of the properties of feeds and their physicochemical status in operating conditions.

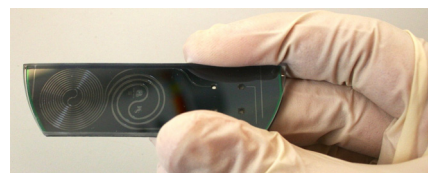
However, their nature and composition – usually complex – make these determinations lengthy and difficult. In addition, during the exploratory phases of R&I projects, these feeds are not necessarily available in sufficiently large quantities to be characterized using conventional tools.

A solution: microfluidics^b. Therefore, by miniaturizing tools to determine thermodynamic properties (phase diagram, density, viscosity), the amount of product used is very limited and results are obtained more quickly⁽¹⁾.

The system we have favored is the silicon/pyrex microchip^c (figure). It accepts a broad range of chemical products at P-T (200 bars/400°C) conditions typical

of conversion processes. Compared with conventional systems, this method has made it possible to determine the supercritical points of “real feed/hydrogen/solvent” mixtures with acquisition times that are reduced five-fold⁽²⁾, a lower cost and sufficient precision to supply data both for experiments on pilot units and process simulation^d.

After having developed a microfluidics test bench for the acquisition of thermodynamic data, research conducted in collaboration with the ICMCB^e aims to explore the potential of this technology for the assessment of homogeneous catalysts and the separation of reaction products. ■



Microfluidics chip for the acquisition of thermodynamic data.

- a - Processes aimed at breaking down large hydrocarbon molecules in order to obtain lighter products.
- b - Science of manipulating minute volumes of fluids, with at least one characteristic dimension in the region of a micrometer.
- c - A silicon wafer engraved with channels and covered with a pyrex plate.
- d - This research was awarded the International Society for Advancement of Supercritical Fluids' 2016 thesis prize.
- e - Institut de chimie de la matière condensée de Bordeaux.

[1] B. Pinho, S. Girardon, F. Bazer-Bachi, G. Bergeot, S. Marre, C. Aymonier, *The Journal of Supercritical Fluids* 2015.

DOI: 10.1016/j.supflu.2015.04.016

[2] B. Pinho, S. Girardon, F. Bazer-Bachi, G. Bergeot, S. Marre, C. Aymonier, *Lab on a chip* 2014, 14 (19), 3843–3849.

DOI: 10.1039/c4lc00505h.

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A digital twin for *in silico* experiments

The catalysts developed by IFPEN are often used in fixed-bed reactors where their grains are packed randomly. For testing them in pilot units, one of the challenges is to guarantee representativity at lower cost, and at the same time improving repeatability. It is therefore important to ensure that both a satisfactory reactor configuration and a filling procedure can be proposed.

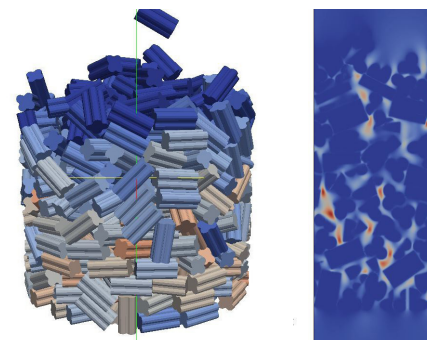
To assess the uncertainties associated with random effects, a switch to virtual (*in silico*) experiments has been suggested. To this end, numerical tools have been developed capable of simulating reacting flows in fixed-bed reactors, on a local scale. Given the fine mesh required and the representative dimensions of our systems, current calculation powers make it possible to simulate our usual reactors with a diameter of around 15 mm.

The first step in a calculation is the simulation of catalyst packing using the Grains3D code⁽¹⁾ (figure). The next step involves calculating the flow of the fluid

in the space between the grains, using the PeliGRIFF code⁽²⁾ (figure). For mass and heat transfer calculations, solvers have been developed on the basis of OpenFOAM, open source library.

Thanks to these developments, IFPEN has operational tools to perform virtual experiments. The first calculations including both thermal and mass transfer data have confirmed the relevance of these technical choices.

The research under way is focusing on the identification of criteria for mesh convergence. In the short term, the simulation of even smaller reactors is planned, along with the definition of a criterion concerning the effects of catalyst dilution. ■



Simulation of a flow in a fixed-bed reactor: catalyst packing (left) and velocity field (right).

[1] M. Rolland, A.D. Rakotonirina, A. Devouassoux, J. L. Barrios Goicetty, J. Y. Delenne & A. Wachs, 2019. Predicting average void fraction and void fraction uncertainty in fixed beds of poly-lobed particles. Accepted in IECR.

[2] F. Dorai, C. M. Teixeira, M. Rolland, E. Climent, M. Marcoux & A. Wachs. 2015. CES, 129, 180-192

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Operando spectroscopy in full transparency

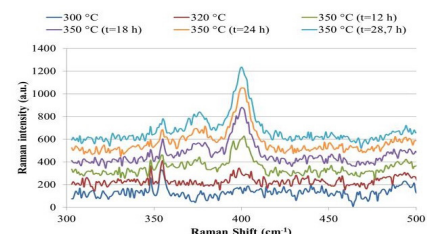
The purification of oil feeds for obtaining clean fuels, as well as the treatment of bio-based feeds that can be incorporated in diesel fuels, rely on the hydrotreatment process and hence on the efficiency of the catalysts used. The latter are the subject of ongoing research to gain a clearer understanding of how they work and improve their performance, in order to reduce the environmental footprint of refining operations. However, current analytical techniques are not capable of characterizing catalysts in their extremely restrictive industrial use conditions (30 to 70 bars, 320 to 380°C).

To overcome this obstacle, an original solution has been found, consisting in miniaturizing a transparent fixed-bed reactor that is then placed inside a Raman spectrometer. This analysis method is conventionally used to characterize catalysts outside units^a. In parallel with the challenge of designing a transparent mini-reactor able to withstand high pressures and temperatures, the “measurement” part required a methodological development in order to be able to precisely focus

the Raman beam on the chosen target (solid or liquid)⁽¹⁾.

The new system makes it possible - for the first time - to obtain spatial and temporal profiles of solid and liquid phases, during the catalyst activation step^b and during diesel fuel hydrotreatment reactions. For the activation study, for example, it was possible to determine the impact of the liquid feed on the kinetics, as well as the evolution of oxide and sulfide phases (figure).

The tool offers significant potential for studying the various catalytic systems used in refining, in process conditions. ■



Raman spectra acquired with a 532 nm laser, power 16mW.

Temporal follow-up of the active phase (MoS₂ at 375 and 400 cm⁻¹) during the activation of a calcined CoMoP catalyst under a [diesel + DMDS] mixture.

[1] M. D. S. Duarte, M. Rolland, C. Sagnard, D. Suire, F. Flacher, O. Delpoux & C. P. Lienemann. A 3 MPa, 350°C transparent fixed bed reactor for operando gas-liquid reaction follow-up. Accepted for publication in Chemical Engineering & Technology.

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a - At atmospheric pressure and room temperature.
b - Transformation of the oxide phase into active sulfide phase.

InSPIRed process control

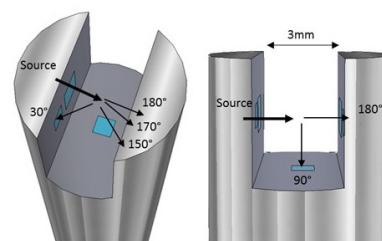
R&D work in the field of process monitoring aims to gain a better understanding of the phenomena involved, increase productivity and enhance safety. In this context, Near Infrared Spectroscopy (NIRS), combined with multivariate data analysis^a, offers a number of advantages for monitoring processes. This non-destructive and rapid technique requires little or no sample preparation and can be used relatively easily for on-line measurement.

The value of NIRS resides in its capacity to provide both physical (relative to diffusion) and chemical (relative to absorption) information about the product, thanks to the interaction between light and matter. However, in the case of heterogeneous and/or complex media, this information is combined and the measurement of the signal at a single point may prove to be insufficient.

To overcome this difficulty, one of the solutions is to have access to several measurements, by reflection and/or transmission at different angles (figure), and to apply appropriate multivariate analysis methods to the spectra obtained. With this in mind, multipoint NIRS was evaluated on several cases.

For example, during the peptization of boehmite^b in an environment representative of industrial conditions, in situ real-time monitoring made it possible to determine the key parameters. In another field, multipoint NIRS was used to determine the cold properties of crude oil, resulting in a patent. Similarly, for the on-line monitoring of products that evolve significantly over time: changing from a clear to a turbid state, for example. This was verified during the monitoring of silica precipitation^(1,2).

These studies have made it possible to verify that multipoint measurements using NIRS provide more information on heterogeneous media, and at the same time improving precision. Consequently they are increasingly being studied for the monitoring of IFPEN's pilot units. ■



Schematic diagram of an immersion probe with measurements at different angles.

- a - Statistical methods for the simultaneous observation and treatment of several statistical variables with a view to identifying relevant synthetic information.
- b - Step in the manufacture of alumina catalyst supports.

[1] M. Rey-Bayle, R. Bendoula, S. Henrot, K. Lamiri, F. Baco-Antonioli, N. Caillol, A. Gobrecht, J. M. Roger. *Analytical and bioanalytical chemistry* 2017. DOI:10.1007/s00216-016-0064-1

[2] M. Rey-Bayle, R. Bendoula, N. Caillol, J. M. Roger. *Journal of Near Infrared Spectroscopy* 2019. Submission accepted.

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News

• **A record of 188 basic patent applications for IFPEN in 2018**, including 88 in the field of New Energy Technologies (NETs).

• By order of the Minister for Higher Education, Research and Innovation, **Jean-Luc Duplan**, a former IFPEN employee, has been appointed deputy regional representative for Research and Technology for the Auvergne-Rhône-Alpes region within the DRRT (regional research and technology delegation).

• **IFPEN's scientific policy is expressed in a video** (YouTube, IFPEN channel), presenting its collaborative research strategy, in the form of interviews with scientific personalities in particular.

• **The open access plug im! platform**, developed by IFPEN, is dedicated to the processing and analysis of signals, images and 3D volumes. It is available to the scientific community as a whole, on YouTube IFPEN channel.

Awards

• **The 2018 Yves Chauvin prize was awarded to Aurélie Pirayre** for her thesis entitled "Reconstruction and clustering with graph optimization and priors on gene networks and images".

• **Céline Pagis**, a young IFPEN researcher in Catalysis, Biocatalysis and Separation was given the L'Oréal-Unesco 2018 "For Women in Science" fellowship.

• **Léo Agélas** and **Guillaume Enchéry**, IFPEN researchers in Applied Mathematics, were awarded the University of Stuttgart prize for their paper on the "Convergence of nonlinear finite volume schemes for heterogeneous anisotropic diffusion on general meshes", published in the *Journal of Computational Physics*.

• IFPEN researcher **Matthieu Mascle** received the "Best Young Professional Paper 2018" prize from the Society of Core Analysts (SCA) for his paper on "In-situ investigation of aging protocol effects on relative permeability measurements using high throughput experimentation methods".

Publications

• The prestigious *Catalysis Science and Technology* journal has published "From sequential chemoenzymatic synthesis to integrated hybrid catalysis: Taking the best of both worlds to open up the scope of possibilities for a sustainable future", a paper co-authored by IFPEN researchers.

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